JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

CuI/Oxalic Diamide Catalyzed Coupling Reaction of (Hetero)Aryl Chlorides and Amines

Wei Zhou,[†,§] Mengyang Fan,[†,§] Junli Yin,[‡] Yongwen Jiang,[†] and Dawei Ma*[,†,‡]

[†]State Key Laboratory of Bioorganic and Natural Products Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China

[‡]School of Physical Science and Technology, ShanghaiTech, 319 Yueyang Road, Shanghai 200031, China

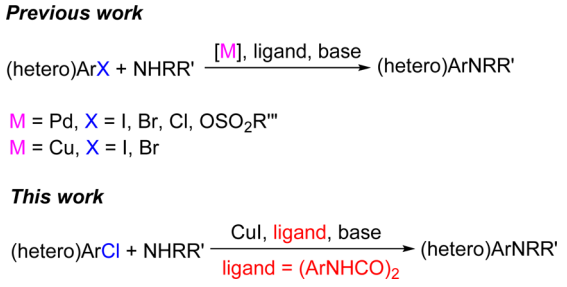
Supporting Information

ABSTRACT: A class of oxalic diamides are found to be effective ligands for promoting CuI-catalyzed aryl amination with less reactive (hetero)aryl chlorides. The reaction proceeds at 120 °C with K_3PO_4 as the base in DMSO to afford a wide range of (hetero)aryl amines in good to excellent yields. The bis(*N*-aryl) substituted oxalamides are superior ligands to *N*-aryl-*N*′-alkyl substituted or bis(*N*-alkyl) substituted oxalamides. Both the electronic nature and the steric property of the aromatic rings in ligands are important for their efficiency.

N-Aryl amine moieties are important structural features that are ubiquitously found in numerous natural products, pharmaceuticals, agrochemicals, and material molecules.[1] A typical approach for preparing *N*-aryl amines is the copper-catalyzed Ullmann coupling reaction of aryl halides with amines.[2] Traditionally, the reaction required a high reaction temperature and the stoichiometric amount of copper reagent, which greatly limited the reaction scope.[2] During the past two decades, two breakthroughs have appeared to overcome these drawbacks. One is the development of palladium-catalyzed coupling of aryl halides with amines using sterically hindered phosphine ligands (Buchwald−Hartwig reaction).[3] Another one is the discovery of efficient bidentate ligands that have promoted copper-catalyzed Ullmann-type reactions.[4−16] These progresses have greatly extended the reaction scope of aryl aminations and allowed these reactions to proceed under mild conditions. Thanks to these advances, the aryl aminations have been intensively applied in the synthesis of functional molecules by researchers in both academia and industry.[3f−k,16,17] However, further breakthroughs are required to make these reactions more attractive. In Cu/ligand-catalyzed aryl amination reaction, one key problem is that less expensive aryl chlorides are still poor substrates,[5,18] which has been considered for years as the weakness of such method in comparison with Buchwald−Hartwig reaction.[3k,16] In consideration of the relative low cost of catalysts and ligands in copper-catalyzed aryl aminations, it is highly desirable that a copper catalyst can sufficiently activate aryl chloride substrates. Herein, we wish to disclose our results by discovering oxalic diamides as powerful ligands for copper catalysis. With these ligands, the amination of (hetero)aryl chlorides could proceed under mild conditions with CuI as the catalyst (Scheme 1).

In search of effective ligands for Cu-catalyzed coupling reactions, we realized that the electronic nature of the ligands

Scheme 1. Coupling Reactions of (Hetero)Aryl Halides with Amines under the Catalysis of Palladium and Copper Complexes



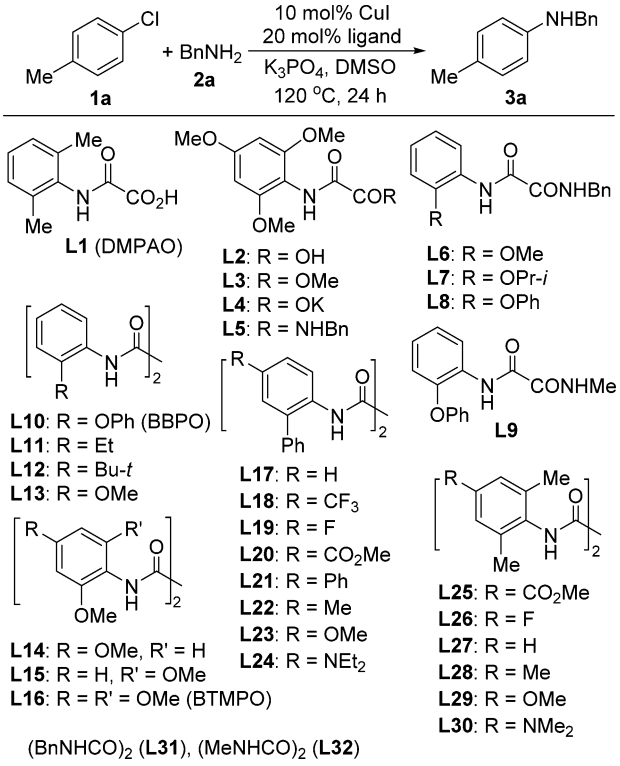
are particularly important for their efficiency.[19] We therefore became interested in developing aromatic bidentate ligands because their electronic nature can be finely tuned by introducing different substituents on the aromatic rings.[19b−d] In 2012, we revealed that 2-(2,6-dimethylphenylamino)-2-oxoacetic acid (DMPAO) effectively promoted CuI-catalyzed N-arylation of acyclic secondary amines that were considered as the difficult substrates previously,[19b] but as well as primary amines even at low catalytic loadings. Its excellent reactivity prompted us to challenge the Cu-catalyzed aryl amination of aryl chlorides. Accordingly, we conducted a CuI/DMPAO catalyzed coupling of 4-methylphenyl chloride with benzylamine and found that reaction occurred at 120 °C in DMSO under the assistance of K_3PO_4, albeit with a low conversion (Table 1, entry 1). Changing the ligand with a more electron-rich 2-(2,4,6-trimethoxyphenylamino)-2-oxoacetic acid (**L2**) gave a similar result (entry 2). Surprisingly, its methyl ester (**L3**) could dramatically increase the conversion to afford arylamine **3a** in 74% yield (entry 3). Since the corresponding potassium salt **L4** still gave a low yield of **3a** (entry 4), we thought that this salt should not be the active ligand. After examining the reaction mixture carefully, we found that **L3** was indeed converted into the corresponding diamide **L5** during the coupling reaction. When **L5** was directly used, coupling product **3a** was obtained in 75% yield (entry 5), indicating that this oxalic diamide is a real ligand for coupling reaction.

In response to this exciting result, we explored the structure−efficiency relationship of a number of oxalic diamides. Thus, **L6**−

Received: August 9, 2015
Published: September 9, 2015

DOI: 10.1021/jacs.5b08411
J. Am. Chem. Soc. 2015, 137, 11942−11945

Table 1. CuI-Catalyzed Coupling of 4-Methylphenyl Chloride with Benzylamine under the Assistance of Different Ligands[a]



entry	ligand	yield (%)[b]	entry	ligand	yield (%)[b]
1	**L1**	15	21	**L21**	77
2	**L2**	16	22	**L22**	87
3	**L3**	74	23	**L23**	88
4	**L4**	10	24	**L24**	92
5	**L5**	75	25[c]	**L25**	21
6	**L6**	62	26[c]	**L26**	49
7	**L7**	74	27[c]	**L27**	65
8	**L8**	73	28[c]	**L28**	69
9	**L9**	56	29[c]	**L29**	92
10	**L10**	86	30[c]	**L30**	94
11	**L11**	45	31	**L31**	61
12	**L12**	17	32	**L32**	11
13	**L13**	66	33[d]	**L16**	84
14	**L14**	73	34[e]	**L16**	78
15	**L15**	82	35[f]	**L16**	49
16	**L16**	92	36[g]	**L16**	29
17	**L17**	76	37[h]	**L16**	65
18	**L18**	23	38[i]	**L16**	48
19	**L19**	61	39[j]	**L16**	38
20	**L20**	48	40[k]	**L16**	91 (89)[l]

[a]General conditions: **1a** (0.5 mmol), **2a** (0.75 mmol), CuI (0.05 mmol), ligand (0.1 mmol), base (1 mmol), solvent (1.0 mL), 120 °C, 24 h. [b]The yield was determined by ^{1}H NMR analysis of crude products using CH_2Br_2 as the internal standard. [c]The reaction was conducted at 115 °C with 5 mol % CuI, 10 mol % ligand, and 110 mol % K_3PO_4. [d]DMF as the solvent. [e]DMA as the solvent. [f]MeCN as the solvent. [g]*t*-BuOH as the solvent. [h]Cs_2CO_3 as the base. [i]K_2CO_3 as the base. [j]Na_2CO_3 as the base. [k]5 mol % CuI, 5 mol % ligand, and 100 mol % K_3PO_4 were used. [l]Isolated yield.

L13 were synthesized from the corresponding monosubstituted anilines. Screening of these ligands demonstrated that 2-methoxyaniline derived diamide **L6** was still active to provide **3a** in 62% yield (entry 6), while improved yields were obtained by employing isopropoxy and benzoxy substituted ligands (entries 7 and 8), presumably because their larger substituents at the *ortho*-position of anilines could prevent the hydrolysis of the ligands.[20]

Changing the *N*-benzyl of **L8** to *N*-methyl led to formation of **3a** in a decreased yield (entry 9). However, complete conversion was observed when *N*,*N*′-bis(2-benzoxyphenyl)-oxalamide (BBPO, **L10**) was utilized (entry 10), which implied that bis(*N*-aryl) substituted oxalamides are more effective ligands. Further investigations indicated that electronic nature of the aromatic ring in ligands played an important role for their efficiency. When the benzoxy group in **L10** was replaced with less electron-rich ethyl and *t*-butyl groups, ligands **L11** and **L12** gave poor results (compare entries 10−12). The similar trend could be seen from the performance of ligands **L13**−**L16** (entries 13−16). The better result obtained by **L15** in comparison with **L14** showed again that increased steric hindrance is necessary to get more effective ligands, while the best result was observed in the case of more electron-rich *N*,*N*′-bis(2,4,6-trimethoxyphenyl)-oxalamide (BTMPO, **L16**) as the ligand (entry 16). To fully demonstrate the importance of the electronic nature in the ligands, we also examined two series of ligands **L17**−**L24** and **L25**−**L30**. The results clearly showed that ligands generated from more electronic-rich anilines are more effective (compare entries 17−24 and entries 25−30). Additionally, decreased yields were obtained by using **L31** and **L32** indicating that aniline-derived diamides were better than aliphatic amine-derived diamides (entries 31 and 32), and such subtle change in electronic nature of the ligands provided significant influence on their efficiency. Noteworthy is that no coupling occurred under similar conditions if the oxalic diamide ligands were switched with other ligands such as amino acids,[4] diamines,[5] salicylaldoxime,[6] 1,10-phenanthroline,[7] diethyl-salicylamide,[8] 1,3-diketones,[9] pyrrole 2-carboxylic acid,[10] *rac*-BINOL,[11] 2-dimethylaminoethanol,[12] *β*-keto esters,[13] 8-hydroxyqunioline,[14] and 2-pyridinyl-*β*-ketones.[15]

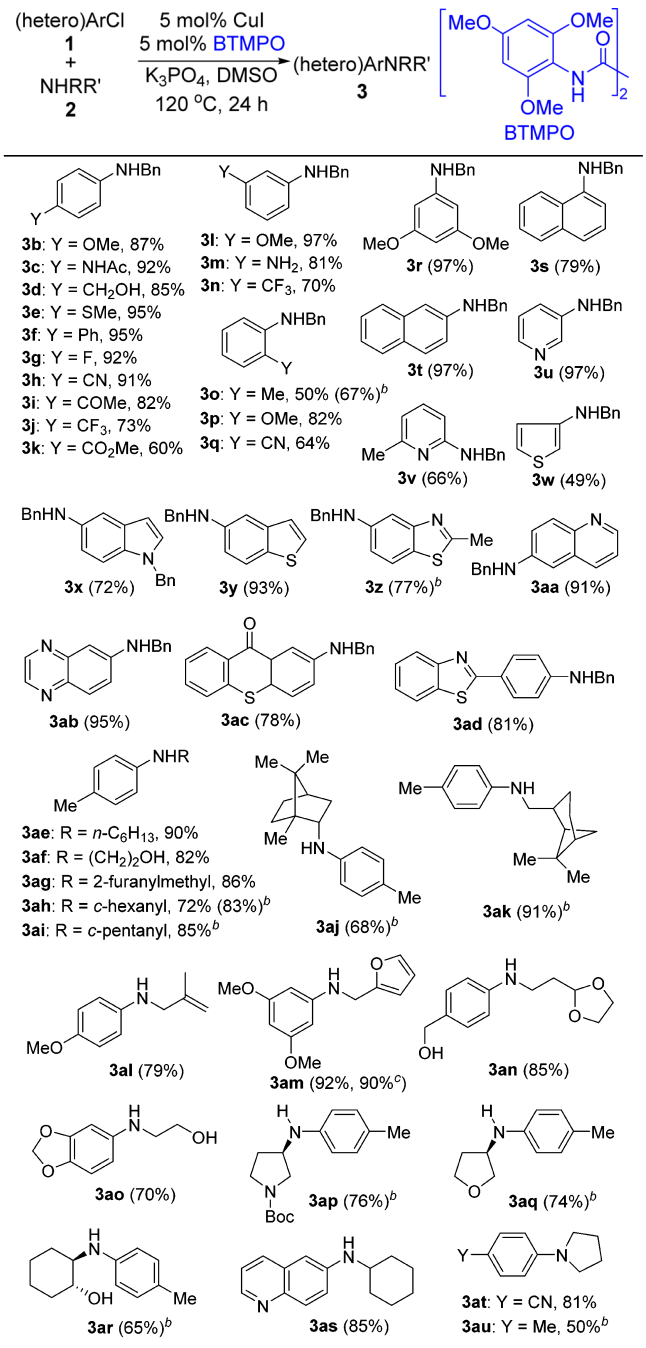
Using **L16** as the ligand, we tested other solvents and bases. Using DMF and DMA only slightly decreased the reaction yields, while much lower yields were observed in cases of MeCN and *t*-BuOH as the solvents (entries 33−36). Change of the base to Cs_2CO_3, K_2CO_3, and Na_2CO_3 also gave poorer results (entries 37−39). Thus, we concluded that the best conditions are K_3PO_4 as the base and DMSO as the solvent. To our delight, under these conditions a 89% isolated yield was obtained, even the loadings of both catalyst and ligand were reduced to 5 mol % (entry 40).

With the optimized conditions in hand, we next explored the reaction scope and limitations by varying aryl chlorides and amines, and the results are summarized in Table 2. We were pleased that a series of *para*-substituted aryl chlorides bearing either electron-donating or electron-withdrawing groups worked well, delivering the coupling products **3b**−**3k** in 60−96% yields. Three *meta*-substituted aryl chlorides were also good substrates, affording **3l**−**3n** in 70−97% yields. The formation of **3m** as a single product implied that chemoselectivity could be obtained between aromatic amines and aliphatic amines. Coupling with sterically hindered *ortho*-substituted aryl chlorides was found to be relatively difficult, and increasing the ligand loading and prolonging reaction time were required to ensure a good yield (for **3o**). The similar trend was also observed from the reactivity difference between 1-naphthyl chloride (**3s**) and 2-naphthyl chloride (**3t**).

A variety of biologically interesting heteroaryl amines could be assembled from the corresponding heteroaryl chlorides using the

DOI: 10.1021/jacs.5b08411
J. Am. Chem. Soc. 2015, 137, 11942−11945

Table 2. Scope of CuI/BTMPO Catalyzed Coupling Reaction of (Hetero)Aryl Chlorides with Amines[a]



[a]General conditions: **1** (1 mmol), **2** (1.5 mmol), CuI (0.05 mmol), BTMPO (0.05 mmol), K_3PO_4 (1.0 mmol), DMSO (1.0 mL), 120 °C, 24 h, isolated yield. [b]The reaction was conducted with 5 mol % CuI and 10 mol % BTMPO for 48 h. [c]Reaction was conducted with 20 mmol of aryl chloride, 2.5 mol % CuI, and 2.5 mol % BTMPO at 120 °C.

present method. These aromatic heterocycles include pyridine (**3u**, **3v**), thiophene (**3w**), protected indole (**3x**), benzothiophene (**3y**), benzothiazole (**3z**), quinoline (**3aa**), and quinoxaline (**3ab**). Furthermore, two aryl chlorides with the additional heterocycles underwent the coupling smoothly, providing arylamines **3ac** and **3ad** in 78% and 81% yields, respectively.

In terms of amine coupling partners, the use of substrates with a long alkyl chain (**3ae**), hydroxyl (**3af**, **3ao**, **3ar**), furanyl (**3ag**, **3am**), cyclic alkyl (**3ah**−**3ak**, **3ap**−**3as**), vinyl (**3al**), ketal (**3an**), and carbamate (**3ap**) groups was found to give the aryl amination products in good to excellent yields. This fact, together with its compatibility with a wide range of functional groups such as amide, thioether, cyano, ketone, ester, trifluoro, amine, and heterocycles that was observed during varying (hetero)aryl chlorides, makes the present method a reliable and attractive approach for assembling (hetero)aryl amines.

The present reaction was quite sensitive to steric hindrance of amines, as evident from the different reactivity displayed by linear alkylamines and cyclic alkylamines (compare **3ae**, **3af** with **3ah**, **3aj**). For cyclic alkylamines, reactions needed higher ligand loadings and longer times to give complete conversion. Another evidence came from the aryl amination with secondary amines. Only 50% yield of **3au** was observed when coupling of 4-methylphenyl chloride with pyrrolidine, a rather reactive secondary amine. Further improvements by using suitable ligands are required to solve this problem. Interestingly, when sterically hindered amines were utilized, electron-poor aryl chlorides were found to be more reactive than electron-rich aryl chlorides (compare **3ah**, **3at** with **3as**, **3au**).

In conclusion, oxalic diamides are discovered to be effective ligands that have enabled the CuI-catalyzed amination of less reactive (hetero)aryl chlorides under relative mild conditions. A wide range of functionalized (hetero)aryl chlorides and amines were compatible with the present reaction conditions, thereby allowing the synthesis of (hetero)aryl amines with diverse structural features. More importantly, oxalic diamide ligands are quite cheap, conveniently available, and easily tunable. These remarkable features make this method very attractive for the preparation of (hetero)aryl amines. Unlike previous investigations on ligand-promoted copper-catalyzed Ullmann-type reactions where only limited ligands were employed from commercial resources and little or no information was able to be collected for its structure−activity relationship,[21] the present investigation has demonstrated the potential to gain the structure−activity relationship of ligand for copper-catalyzed reaction and allowed us to discover more effective ligands through such structural modifications. This finding may stimulate further ligand design for Cu-catalyzed arylation reactions. The mechanistic studies and application of these ligands in other coupling reactions are actively pursued in our laboratory, and the results will be disclosed in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b08411.

Experimental procedures and compound characterization (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*madw@sioc.ac.cn

Author Contributions

§W.Z. and M.F. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful to Chinese Academy of Sciences and the National Natural Science Foundation of China (grant 21132008

DOI: 10.1021/jacs.5b08411
J. Am. Chem. Soc. 2015, 137, 11942−11945

& 20921091) for their financial support, and Xiangyang Feng and Xi Jiang for synthesizing some ligands.

REFERENCES

(1) For selected books and reviews, see: (a) Craig, P. N. In *Comprehensive Medicinal Chemistry*; Drayton, C. J., Ed.; Pergamon Press: New York, 1991. (b) Lawrence, S. A. *Amines: Synthesis, Properties and Application*; Cambridge University Press, Cambridge, 2004. (c) Horton, D. A.; Bourne, G. T.; Smythe, M. L. *Chem. Rev.* **2003**, *103*, 893−930. (d) Lygaitis, R.; Getautic, V.; Grazulevicius, J. V. *Chem. Soc. Rev.* **2008**, *37*, 770−788. (e) Liang, M.; Chen, J. *Chem. Soc. Rev.* **2013**, *42*, 3453−3488.

(2) (a) Ullmann, F. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 2382. For reviews, see: (b) Linsley, J. *Tetrahedron* **1984**, *40*, 1433−1456. (c) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359−1469.

(3) (a) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1348−1350. (b) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609−3612. For reviews, see: (c) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046−2067. (d) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805. (e) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852−860. (f) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768−2813. (g) Surry, D. S.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 6338−6361. (h) Hartwig, J. F. *Acc. Chem. Res.* **2008**, *41*, 1534−1544. (i) Torborg, C.; Beller, M. *Adv. Synth. Catal.* **2009**, *351*, 3027−3043. (j) Surry, D. S.; Buchwald, S. L. *Chem. Sci.* **2011**, *2*, 27−50. (k) Bariwal, J.; Van der Eycken, E. *Chem. Soc. Rev.* **2013**, *42*, 9283−9303.

(4) (a) Ma, D.; Zhang, Y.; Yao, J.; Wu, S.; Tao, F. *J. Am. Chem. Soc.* **1998**, *120*, 12459−12467. (b) Ma, D.; Cai, Q.; Zhang, H. *Org. Lett.* **2003**, *5*, 2453−2455. (c) Zhang, H.; Cai, Q.; Ma, D. *J. Org. Chem.* **2005**, *70*, 5164. (d) Guo, X.; Rao, H.; Fu, H.; Jiang, Y.; Zhao, Y. *Adv. Synth. Catal.* **2006**, *348*, 2197−2202. (e) Zou, B.; Yuan, Q.; Ma, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 2598−2601.

(5) (a) Klapars, A.; Antilla, J. C.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2001**, *123*, 7727−7729. (b) Klapars, A.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 7421−7428.

(6) (a) Cristau, H.-J.; Cellier, P. P.; Hamada, S.; Spindler, J.-F.; Taillefer, M. *Chem. - Eur. J.* **2004**, *10*, 5607−5622. (b) Cristau, H.-J.; Cellier, P. P.; Hamada, S.; Spindler, J.-F.; Taillefer, M. *Eur. J. Org. Chem.* **2004**, *2004*, 695−709.

(7) Goodbrand, H. B.; Hu, N.-X. *J. Org. Chem.* **1999**, *64*, 670−674.

(8) Kwong, F. Y.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 793−796.

(9) (a) Buck, E.; Song, Z. J.; Tschaen, D.; Dormer, P. G.; Volante, R. P.; Reider, P. J. *Org. Lett.* **2002**, *4*, 1623−1626. (b) Shafir, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2006**, *128*, 8742−8743. (c) Shafir, A.; Lichtor, P. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 3490−3491.

(10) Altman, R. A.; Anderson, K. W.; Buchwald, S. L. *J. Org. Chem.* **2008**, *73*, 5167−5169.

(11) (a) Zhu, D.; Wang, R.; Mao, J.; Xu, L.; Wu, F.; Wan, B. *J. Mol. Catal. A: Chem.* **2006**, *256*, 256−260. (b) Jiang, D.; Fu, H.; Jiang, Y.; Zhao, Y. *J. Org. Chem.* **2007**, *72*, 672−674. (c) Zeng, L.; Fu, H.; Qiao, R.; Jiang, Y.; Zhao, Y. *Adv. Synth. Catal.* **2009**, *351*, 1671−1676.

(12) (a) Lu, Z.; Twieg, R. J.; Huang, S. D. *Tetrahedron Lett.* **2003**, *44*, 6289−6292. (b) Lu, Z.; Twieg, R. J. *Tetrahedron Lett.* **2005**, *46*, 2997−3001. (c) Lu, Z.; Twieg, R. J. *Tetrahedron* **2005**, *61*, 903−918.

(13) Lv, X.; Bao, W. *J. Org. Chem.* **2007**, *72*, 3863−3867.

(14) (a) Liu, L.; Frohn, M.; Xi, N.; Dominguez, C.; Hungate, R.; Reider, P. J. *J. Org. Chem.* **2005**, *70*, 10135−10138. (b) Ueda, S.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2012**, *51*, 10364−10367.

(15) Wang, D. P.; Cai, Q.; Ding, K. *Adv. Synth. Catal.* **2009**, *351*, 1722−1726.

(16) For recent books and reviews, see: (a) Shaughnessy, K. H.; Ciganek, E.; Devasher, R. B. *Organic Reactions (Hoboken, NJ, USA)* **2014**, *85*, 1−668. (b) Sambiagio, C.; Marsden, S. P.; Blacker, A. J.; McGowan, P. C. *Chem. Soc. Rev.* **2014**, *43*, 3525−3550. (c) Jiang, Y.; Ma, D. In *Copper-Mediated Cross-Coupling Reactions*; Evano, G., Blanchard, N., Eds; John Wiley & Sons Inc: Hoboken, NJ, 2013; pp 589−642. (d) Surry, D. S.; Buchwald, S. L. *Chem. Sci.* **2010**, *1*, 13−31. (e) Sperotto, E.; Klink, G. P. M.; Koten, G.; Vries, J. G. *Dalton Trans.* **2010**, *39*, 10338. (f) Monnier, F.; Taillefer, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 6954−6971. (g) Evano, G.; Blanchard, N.; Toumi, M. *Chem. Rev.* **2008**, *108*, 3054−3131.

(17) (a) Coman, S. M.; Parvulescu, V. I. *Org. Process Res. Dev.* **2015**, DOI: 10.1021/acs.oprd.5b00010. (b) Okano, K.; Tokuyama, H.; Fukuyama, T. *Chem. Commun.* **2014**, *50*, 13650−13663. (c) Evano, G.; Theunissen, C.; Pradal, A. *Nat. Prod. Rep.* **2013**, *30*, 1467−1489. (d) Lee, J.; Panek, J. D. In *Copper-Mediated Cross-Coupling Reactions*; Evano, G., Blanchard, N., Eds; John Wiley & Sons Inc, Hoboken, NJ, 2013; pp 589−642. (e) Ribecai, A.; Stabile, P. In *Transition Metal-Catalyzed Couplings in Process Chemistry*; Magano, J., Dunetz, J. R., Eds.; 2013; pp 135−145. (f) Kunz, K.; Lui, N. In *Copper-Mediated Cross-Coupling Reactions*; Evano, G., Blanchard, N., Eds; John Wiley & Sons Inc, Hoboken, NJ, 2013; pp 725−744. (g) Ma, D.; Jiang, Y. *Chimia* **2011**, *65*, 914−918.

(18) For a review, see: Monnier, F.; Taillefer, M. *Top. Organomet. Chem.* **2013**, *46*, 173−204.

(19) (a) Ma, D.; Cai, Q. *Acc. Chem. Res.* **2008**, *41*, 1450−1460. (b) Zhang, Y.; Yang, X.; Yao, Q.; Ma, D. *Org. Lett.* **2012**, *14*, 3056−3059. (c) Yang, X.; Zhang, Y.; Ma, D. *Adv. Synth. Catal.* **2012**, *354*, 2443−2446. (d) Jia, J.; Jiang, C.; Zhang, X.; Jiang, Y.; Ma, D. *Tetrahedron Lett.* **2011**, *52*, 5593−5595.

(20) Hydrolysis of the oxalic diamide ligands during the coupling reaction was detected in some cases, which should be partially responsible for deactivation of the present catalytic system.

(21) Buchwald and co-workers have briefly studied the structure−efficiency relationship of substituted phenanthrolines in their Cu-catalyzed coupling reactions with *N*-heterocycles and phenols. See: (a) Altman, R. A.; Buchwald, S. L. *Org. Lett.* **2006**, *8*, 2779−2782. (b) Altman, A. R.; Koval, E. D.; Buchwald, S. L. *J. Org. Chem.* **2007**, *72*, 6190−6199. (c) Altman, R. A.; Shafir, A.; Choi, A.; Lichtor, P. A.; Buchwald, S. L. *J. Org. Chem.* **2008**, *73*, 284−286.

DOI: 10.1021/jacs.5b08411
J. Am. Chem. Soc. 2015, 137, 11942−11945